

# Preparation of Ru Nanoparticles Supported on $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Its Novel Catalytic Activity for Ammonia Synthesis

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Uniform ruthenium metal nanoparticles with an average diameter of 5 nm were prepared and supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> up to 6.3 wt%. The ruthenium nanoparticles were obtained by the reduction of RuCl<sub>3</sub> in ethylene glycol. While maintaining their original morphology, more than 99% of the colloidal Ru nanoparticles, obtained were successfully supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. The Ru/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from a metal colloid had an unusually high activity for ammonia synthesis. The rate of ammonia formation was at least 12 times higher than the rate of nonpromoted Ru/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by conventional methods, and at least 3.5 times higher than the promoted Cs, Rb, K, Ce, La, and Sm Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. Alumina was not expected to be an ideal support for ammonia synthesis because of its acidity, and thus the promotion by additives was considered necessary. The present investigation proves that alumina can be a suitable support for ammonia synthesis if ruthenium is supported on it as metal nanoparticles. The results point out the possibility that the active sites formed by conventional impregnation methods are significantly contaminated with the supports. In contrast, by keeping the interaction with the support at a minimum, the novel preparation method of the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst by Ru colloid deposition gives well-defined metal particles with high catalytic activity. © 2001 Elsevier Science

**Key Words:** metal nanoparticles; Ru; ammonia synthesis; polyol method; supported catalyst.

## 1. INTRODUCTION

Ruthenium is known to have one of the highest catalytic activities for ammonia synthesis (1). The conventional ruthenium catalysts are prepared by the impregnation of oxide supports either with an aqueous solution of RuCl<sub>3</sub> · 3H<sub>2</sub>O or with Ru<sub>3</sub>(CO)<sub>12</sub> dissolved in tetrahydrofuran (2, 3). When catalysts are prepared by impregnation of alumina with RuCl<sub>3</sub>, the metal particles, after drying, calcination, and reduction, are not uniform in size and shape. The metal particles obtained through the impregnation with Ru<sub>3</sub>(CO)<sub>12</sub> are modeled as Ru<sub>6</sub> clusters. However,

this is still in question, because a raft structure is also suggested (4).

It is well known that the catalytic activity of a supported metal is strongly related to the morphology of the particle, i.e., size and shape (5). However, the conventional preparation of catalysts, consisting of the impregnation of a support with an aqueous solution of a soluble metal precursor, makes it difficult to control the final size and shape of the supported metal particles. Additionally, it is highly possible that the support has a great influence on the catalytic activity of the metal when the catalyst is prepared by impregnation. It has been evidenced that the active phase of catalysts prepared by impregnation can contain variable amounts of aluminum as a result of support dissolution, depending on the conditions of impregnation such as time, temperature, and pH (6, 7). Moreover, very little is known about the structure of small, supported metal particles and their interaction with the support.

The conventional Ru/Al<sub>2</sub>O<sub>3</sub> catalysts are known to exhibit quite low activities for ammonia synthesis, and this has been attributed to the acidity of alumina. The addition of alkali or lanthanide promoters was reported to be an effective way of enhancing the catalytic activity (2, 3). The proposed mechanism of this promoting effect is a contentious issue. Aika *et al.* (8) explained the enhancement of the catalytic activity by electronic promotion. According to the mechanism they proposed, the electrons are transferred from the support to the ruthenium metal, inducing a decrease in the ionization potential of ruthenium. The decreased ionization potential allows electron transfer from the metal to the anti-bonding orbits of the nitrogen atom, reducing the activation energy for dissociative adsorption of the N<sub>2</sub> molecule. On the other hand, LEED and NMR spectroscopy results could not prove such an electron transfer from alkali promoters to ruthenium (9, 10).

An alternative method to obtain supported catalysts with well-defined metal particles is the preparation of supported catalysts from metal colloids. The great advantage of the colloid method is that it provides relatively monodispersed metal particles. Recent investigation shows that not only

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the particle size but also the crystal structure of the metal nanoparticles can be controlled to some extent by using appropriate structure-directing polymers for colloid preparation (11). Additionally, the preparation of supported catalysts from metal colloids can minimize the effect of support on the metallic active phase. However, there are very few reports about a preparation method for a stable Ru colloid. Hirai *et al.* (12, 13) made an attempt to prepare a Ru colloid by refluxing a methanol–water solution containing Ru salts. Although they succeeded in obtaining stable colloid solutions of Rh, Pd, Os, Ir, Ag, and Au by this method, they could not obtain a Ru colloid. Recently, Vidoni *et al.* (14) succeeded in obtaining a stable ruthenium colloid. The method needs high pressure (3 bar of H<sub>2</sub>), a special precursor, and an organic solvent, and thus it is not very convenient for general application.

Recently, the polyol method (15, 16) was reported as new and promising for the preparation of nanoscale metal powders. This method can be applied for all the metal salts that are soluble in ethylene glycol. Using the polyol method, Kurihara *et al.* (16) succeeded in obtaining nanosize powders of more than 10 metals including ruthenium. This method produces a black deposit of metal particles on the bottom of the reactor vessel. The reduction of metal ions takes place in three steps: nuclear formation, particle growth, and aggregation of the particles. The metal powders obtained by the polyol method are the result of the formation of metal particles and their aggregation. If the aggregation is avoided, the polyol method can be applied for the preparation of ruthenium colloids.

The objectives of this paper are (i) to prepare a stable Ru colloid with a sharp size distribution by using the polyol method, (ii) to find the optimum experimental conditions for supporting Ru colloidal particles on  $\gamma$ -alumina, and (iii) to test the catalytic activity of the alumina-supported ruthenium nanoparticles for ammonia synthesis. Additionally, we will discuss the support role played in the formation of catalytic active phases.

## 2. METHODS

### 2.1. Preparation of Ru Colloid

The polyol method was applied to the preparation of a Ru colloid as in the report by Kurihara *et al.* (16). The original polyol method for the synthesis of metal powders was adapted for colloid preparation by decreasing the concentration of metal precursor in the solution. First, the RuCl<sub>3</sub> · *n*H<sub>2</sub>O (Wako Chemicals, purity >99%) was dissolved in ethylene glycol. The temperature of the solution was then increased up to 453 K by using an oil bath. The process of metal reduction was monitored by a TEM and a UV–vis spectrophotometer. A few milliliters of aliquots were sampled periodically from the solution and then cooled down rapidly by using an ice-water bath.

### 2.2. Preparation of Ru/Al<sub>2</sub>O<sub>3</sub>

The alumina used in this study, supplied by Aerosil Japan Co., has a surface area of 123.8 m<sup>2</sup>/g and an average particle size of 13 nm. A ruthenium colloid obtained by the polyol method was supported on  $\gamma$ -alumina by (i) deposition of the Ru colloid, which was already formed, onto alumina; and (ii) reduction of ruthenium chloride in the presence of alumina (on the surface of alumina). In the former case, the Ru colloid was prepared according to the description presented in Section 2.1.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (2 g) was then added to the colloidal solution under vigorous stirring to form a suspension. In the latter case, 2 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was suspended into 50 ml of an ethylene glycol solution of RuCl<sub>3</sub>, and then the temperature of the suspension was increased up to 453 K. In both cases, ethylene glycol was removed later by diluting the suspension with 450 ml of 0.3 M NaNO<sub>3</sub> aqueous solution. The solid was collected by filtration, and then dried in air.

The size of the ruthenium particles and their dispersion were determined by chemisorption of H<sub>2</sub> and CO, assuming that each exposed Ru atom could adsorb one hydrogen atom or one CO molecule. Prior to the chemisorption measurements, the Ru/Al<sub>2</sub>O<sub>3</sub> samples were heated in vacuum up to 673 K, treated with H<sub>2</sub> at 200 Torr for 2 h, evacuated, and then cooled down to room temperature.

### 2.3. Catalytic Activity Measurements

The catalytic activity of Ru/Al<sub>2</sub>O<sub>3</sub> obtained by the polyol method was measured for ammonia synthesis. The catalytic tests were performed at atmospheric pressure in a stainless-steel reactor containing 0.4 g of Ru/Al<sub>2</sub>O<sub>3</sub> (6.3 wt% Ru). Prior to the catalytic tests, the Ru/Al<sub>2</sub>O<sub>3</sub> was pelletized, crushed, and then sieved. The fraction, from 335 to 1000  $\mu$ m, was collected and loaded into the reactor. Before the test, the sample was reduced in H<sub>2</sub> flow at 823 K for 2 h.

The catalytic activity tests were carried out at a flow rate of the reaction mixture 60 cm<sup>3</sup>/min STP (45 cm<sup>3</sup>/min H<sub>2</sub> and 15 cm<sup>3</sup>/min N<sub>2</sub>). The rate of ammonia synthesis was measured in a 638 to 773 K temperature range. The produced ammonia was trapped by a 2 × 10<sup>-3</sup> N solution of sulfuric acid, and the rate of ammonia formation was determined from the decrease in the conductivity of the solution.

### 2.4. Analysis

Several experimental techniques have been used to characterize the samples. The X-ray powder diffraction (XRD) analysis was carried out by using the CuK $\alpha$  radiation of a Rigaku Geiger Flex RAD-B diffractometer.

Transmission electron microscopy (TEM) with electron probe X-ray microanalysis (EPXMA) (Hitachi H8 100) was performed at 200 kV. The liquid samples for TEM were prepared by dropping the solution onto carbon-coated copper-mesh grids (Oken) and drying in air. The solid

samples were grained well with an agate mortar, suspended in water, and then supported on the carbon-mesh grid.

UV-vis spectra were measured by a Hitachi U-2000A spectrophotometer using distilled water as the reference.

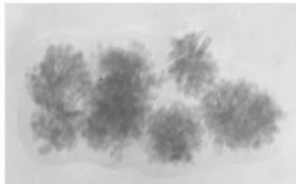

The zeta potential was measured with an electrophoretic light scattering spectrophotometer (Otsuka Electronics ELS-800) using ethylene glycol as the background solution.

The concentration of Ru was determined by an inductively coupled plasma spectrometer (ICP, Seiko SPS 400).

### 3. RESULTS AND DISCUSSION

#### 3.1. Synthesis and Characterization of Ruthenium Colloid

The process of Ru reduction in ethylene glycol was monitored by TEM and a UV-vis spectrophotometer. Figure 1 shows the time change of the solution color together with the corresponding TEM images. The color of the initial solution, i.e., ethylene glycol solution of  $\text{RuCl}_3$ , was yellow. In the course of heating, this color changed to transparent (after 5 min), pink (after 8 min), brown (after 10 min), and finally gray. In the early stages of heating, before the solution became brownish, particle formation could not be observed by TEM. After heating for 10 min, the color of the solution turned to brown, and the formation of small particles was observed. EPXMA proved that the particles were composed of ruthenium, and an electron beam diffraction pattern indicated a crystalline structure of these parti-

time (min)	color	TEM observation
0	yellow	
↓		
~5	transparent	
↓		
~8	pink	
↓		
~10	brown	→ 
↓		
		→ 
~15	gray	→



 25 nm  
 (a) formation of particles  
 100 nm  
 (b) agglomeration

FIG. 1. Schematic time course of the reduction, and TEM observation of the solution.

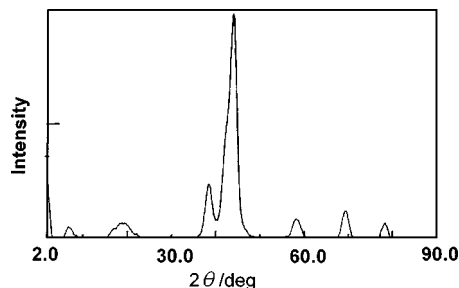


FIG. 2. XRD pattern of the black precipitate.

cles. The primary small particles had a uniform ellipsoidal shape with a diameter of less than 5 nm. Therefore, it can be concluded that the brownish clear solution obtained after 10 min of heating was a colloidal solution of the ruthenium nanoparticles.

Further heating led the colloidal particles to agglomerate. Aggregates of around  $1 \mu\text{m}$  were observed by TEM after 15 min of heating (Fig. 1 (b)). After 30 min of heating, a fine black precipitate was formed at the bottom of the reaction vessel. The XRD pattern of this powder confirmed the complete reduction of  $\text{RuCl}_3$  to Ru metal (Fig. 2).

The polyol method was developed to prepare metal powders. By decreasing the concentration of  $\text{RuCl}_3$  in ethylene glycol by about 1/100, we succeeded in obtaining a stable Ru colloid by the polyol method. The concentration of  $\text{RuCl}_3$  in ethylene glycol and the reduction time were other crucial factors for obtaining a monodispersed and stable Ru colloid. To avoid the agglomeration process, it was necessary to stop the reduction immediately after the formation of the small Ru particles.

The UV-vis spectrum of the freshly prepared ethylene glycol solution of  $\text{RuCl}_3$  exhibited a broad absorption maximum at 398 nm (Fig. 3 (a)). This peak shifted to a shorter wavelength, 328 nm, after 5–8 min of reduction (Fig. 3 (b)). At this reduction time the solution was transparent. It is noteworthy that a new absorption maximum was formed at 275 nm after 8 min of reduction. In this stage the color of the solution turned pink (Fig. 3 (c)). The intensity of the new peak at 275 nm did not change by further heating, whereas the intensity of the peak at 328 nm decreased in time (Fig. 3 (d)). Despite our expectation, we could not find any relationship between the colloid formation and the rise of the peak at 275 nm. This peak may be due to the formation of some intermediate species which appeared during the process of  $\text{RuCl}_3$  reduction. Various Ru species, such as  $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Ru}(\text{H}_2\text{O})_5\text{Cl}]^{2+}$ , or *cis*- and *trans*- $[\text{Ru}(\text{H}_2\text{O})_4\text{Cl}_2]^+$ , have been observed during the reduction of a commercial hydrated ruthenium chloride with mercury (17). The formation of one or more of these species could be the reason for the rise of the peak at 275 nm.

The UV-vis spectrum of the gray colloid showed broad adsorption continua that extend throughout the

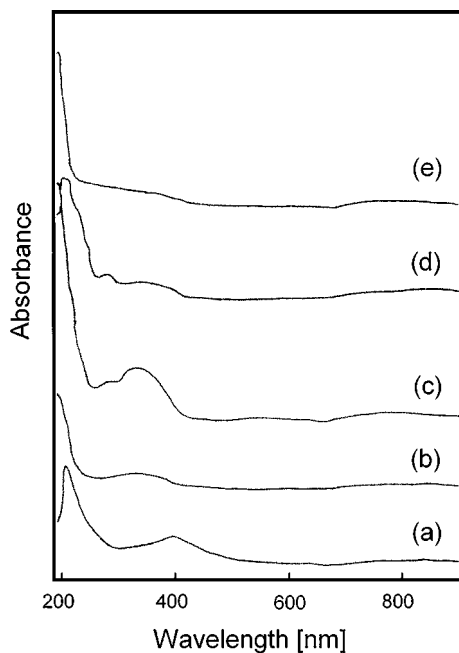


FIG. 3. UV-vis spectra of solution before and after  $\text{RuCl}_3$  reduction. (a) 0 min (before reduction), (b) 5 min, (c) 8 min, (d) 11 min, (e) 15 min.

visible–near-ultraviolet region (Fig. 3 (e)). This spectrum agreed well with the spectrum of the ruthenium colloid having a diameter of 10 nm, which was calculated by means of the Mie theory using the optical constants of the metal (18).

The reduction process of  $\text{RuCl}_3$  in ethylene glycol can proceed in two steps: (i) ligand exchange around the  $\text{Ru}^{3+}$  ions and (ii) reduction of  $\text{Ru}^{3+}$  to Ru metal. When a  $\text{K}_2\text{PtCl}_4$  solution is reduced by  $\text{H}_2$  gas, ligand exchange between  $\text{Cl}^-$  and  $\text{H}_2\text{O}$  takes place, and this is reflected in the change of the UV-vis spectra (19). It is highly possible that the color change from yellow to transparent (Fig. 1) was caused by the ligand exchange taking place prior to the reduction step. In the polyol method, ethylene glycol is not only a solvent but also a reducing agent. The oxidation of ethylene glycol results in the formation of glyoxal ( $\text{CHOCHO}$ ) via glycolaldehyde ( $\text{HOCH}_2\text{CHO}$ ) and/or glycolic acid ( $\text{HOCH}_2\text{COOH}$ ) (20). Our IR measurement did not show the presence of a  $\text{C}=\text{O}$  group. This suggests that ethylene glycol can be easily oxidized to glyoxal, whose boiling point is 324 K.

### 3.2. Supporting Ruthenium Nanoparticles on $\gamma\text{-Al}_2\text{O}_3$

Attempts were made to support the ruthenium nanoparticles, which were obtained by the polyol method, on  $\gamma\text{-Al}_2\text{O}_3$ . As described under Methods two procedures were tried supporting before or after reduction of ruthenium. In the latter case, several difficulties arose. As discussed in Section 3.1, the reduction of  $\text{RuCl}_3$  proceeds quickly, and the solution should be cooled down rapidly after adequate time of reduction to avoid the agglomeration of the particles. In practice, we could not obtain uniform and well-

dispersed Ru nanoparticles on  $\gamma\text{-Al}_2\text{O}_3$  by adding alumina into the suspension of the already formed Ru colloid solution.

The other preparation method consisted of the reduction of  $\text{RuCl}_3$  by ethylene glycol in the presence of alumina. First,  $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$  was dissolved in 50 ml of ethylene glycol, and then 2 g of  $\gamma\text{-Al}_2\text{O}_3$  was added to form a suspension. The experimental conditions, such as temperature and time of reduction, were identical to those described for the preparation of the Ru colloid (Section 2.1). The color of the suspension changed from pale yellow to light brown. The suspension was then cooled down to room temperature. Most of the ethylene glycol was removed by washing the alumina with a  $\text{NaNO}_3$  solution. The solid phase was collected by filtration and dried at room temperature in vacuum.

The concentrations of Ru in the suspension before reduction and in the filtrate were determined by ICP. Table 1 lists the concentrations of Ru in the initial  $[\text{Ru}]_{\text{initial}}$  and final suspensions  $[\text{Ru}]_{\text{final}}$ . By using these data, the concentration of ruthenium on the solid ( $\{\text{Ru}\}_{\text{support}}$ , expressed by weight percent) and the proportion of supported ruthenium, expressed as  $[\text{Ru}]_{\text{support}}/[\text{Ru}]_{\text{initial}}$  were obtained and are listed in Table 1. From Table 1, it can be observed that, by this method, ruthenium was supported on  $\gamma\text{-Al}_2\text{O}_3$  with a remarkably high efficiency. The experimental results confirmed the high reproducibility of this method.

The  $\text{Ru}/\text{Al}_2\text{O}_3$  obtained was observed by TEM. The TEM image shows the presence of many black and dispersed particles on the support (Fig. 4a). The EPXMA measurement proved that the black spots corresponded to ruthenium particles (Fig. 4b). It can be seen that the ruthenium particles were uniform in size and shape, and they were dispersed well on the surface of  $\gamma\text{-Al}_2\text{O}_3$ . Figure 5 shows the size distribution of the ruthenium particles, which was obtained by counting more than 200 particles observed by TEM. The mean particle size of Ru nanoparticles supported on the alumina was 4.3 nm, and this corresponded well the average size of the colloidal Ru nanoparticles (around 5 nm) (Fig. 1).

The sizes of the supported Ru particles obtained by chemisorption of  $\text{H}_2$  and CO were 4.8 and 5.4 nm, respectively. These values agree well with the particle size obtained from TEM observation (Table 2). In reality, Ru metal can chemisorb up to 2 mol of CO/mol, resulting in dicarbonylated ruthenium species anchored to alumina.

TABLE 1

#### Ru Concentration at the Initial and Final Stages of the Reduction

$[\text{Ru}]_{\text{initial}}$ (mmol/L)	$[\text{Ru}]_{\text{final}}$ ( $\mu\text{mol/L}$ )	$\{\text{Ru}\}_{\text{support}}$ (Wt%)	$[\text{Ru}]_{\text{support}}/[\text{Ru}]_{\text{initial}}$ (%)
16.9	76.7	6.29	99.5

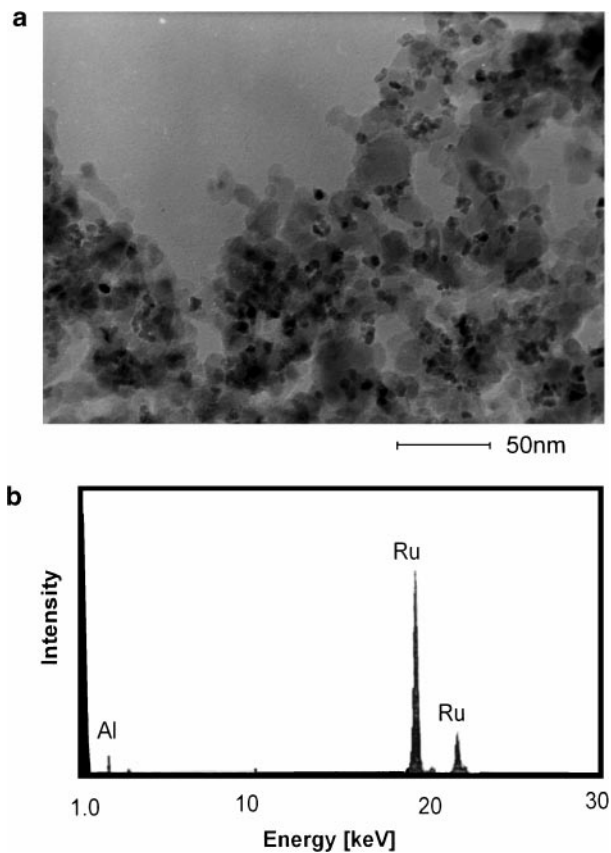


FIG. 4. (a) TEM image and (b) EPXMA spectrum of 6.3 wt% Ru/ $\gamma$ - $\text{Al}_2\text{O}_3$ .

This was observed especially in the case of very small ruthenium clusters prepared from  $\text{Ru}_3(\text{CO})_{12}$  (21). On the other hand, the large ruthenium clusters are less reactive against CO, chemisorbing up to 1.4 mol of CO/mol of metal (21). From the results shown in Table 2, it can be said that the ratio between adsorbed CO/H was around 1:1, and this means that the supported ruthenium nanoparticles have lower reactivity against CO. Therefore, it was reasonable to suppose that each exposed Ru atom adsorbed one hydrogen atom or one CO molecule.

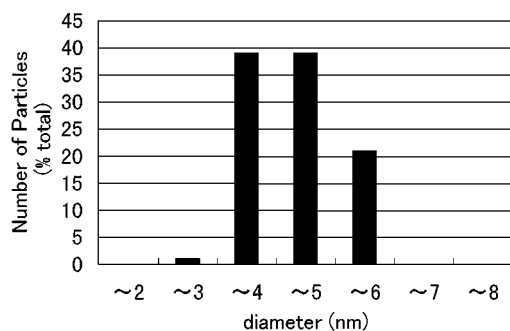


FIG. 5. Size distribution of ruthenium particles on  $\text{Al}_2\text{O}_3$  as determined from TEM micrographs.

TABLE 2

Size of Ru Nanoparticles (nm) Measured by Different Methods

	TEM	$\text{H}_2$ chemisorption	CO chemisorption
Ru colloid	5	—	—
Ru/ $\text{Al}_2\text{O}_3$ (before reaction)	4.3	4.8	5.4
Ru/ $\text{Al}_2\text{O}_3$ (After reaction)	—	5.1	—

These results suggest that the polyol method has an advantage in obtaining supported Ru catalysts, which have uniform and well-dispersed particles. A good dispersion of Ru particles on an 8 wt% Ru catalyst was obtained from a  $\text{Ru}_3(\text{CO})_{12}$  precursor (21). However, in practice it is difficult to obtain highly dispersed Ru particles by a conventional preparation method using  $\text{RuCl}_3$  as a precursor. Moreover, it is noteworthy that in the case of the polyol method, metal loading onto the support can be increased up to 6.3 wt% or more (reported in the following) without affecting the particle size and dispersion.

To reveal the supporting mechanism of the Ru nanoparticles on  $\gamma$ - $\text{Al}_2\text{O}_3$ , the zeta potential of the ruthenium colloid was measured by using an electrophoretic light scattering spectrophotometer. The sample for this measurement was prepared without alumina, and ethylene glycol was used as the reference solution. The pH values of the obtained colloid were adjusted by adding HCl or NaOH solutions. Figure 6 shows the zeta potential of a ruthenium colloid obtained by the polyol method. It can be seen that the Ru colloid is negatively charged at a pH below 8. When the ethylene glycol solution of  $\text{RuCl}_3$  was reduced together with  $\gamma$ - $\text{Al}_2\text{O}_3$ , the pH value of the resultant solution was 5. In this case, the Ru colloid was negatively charged as shown in Fig. 6. On the other hand, the  $\text{pH}_{\text{ZPC}}$  of the  $\gamma$ - $\text{Al}_2\text{O}_3$  used in our study was reported to be 8 (6). Therefore, the surface of alumina must be positively charged at pH 5. In conclusion it can be said that the ruthenium particles, formed in ethylene glycol solution, were supported on  $\gamma$ - $\text{Al}_2\text{O}_3$  by electrostatic force. This is also supported by additional experiments using a surfactant, poly(vinyl alcohol). Using this

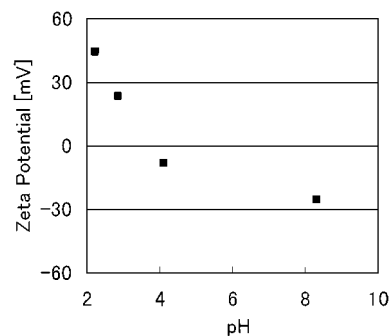


FIG. 6. Zeta potential of ruthenium colloid.

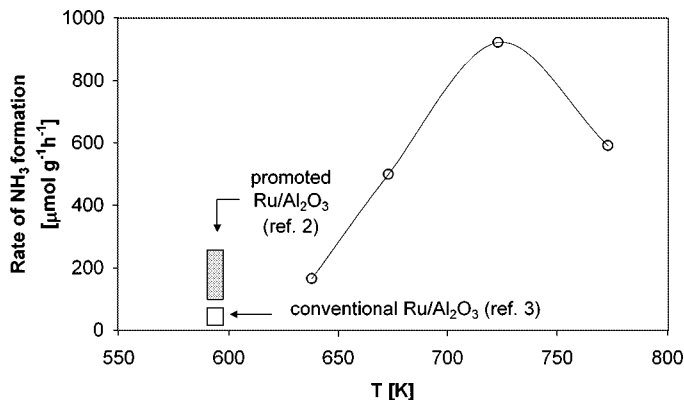


FIG. 7. Temperature dependence of the rate of ammonia synthesis over Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (6.3 wt%). The rates over conventional Ru/Al<sub>2</sub>O<sub>3</sub> catalysts are also shown for comparison.

nonionic surfactant, the concentration of ruthenium on the solid decreased from 6.3 to 4.7 wt%, although the condition was the same. Polymers are known to cap the surface of colloid particles. This phenomenon is known as steric stabilization (22). By capping poly(vinyl alcohol), the distance between the Ru metal particles and the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> increased, and therefore the Coulombic force between them decreased inversely proportional to the second power of the distance.

### 3.3. Catalytic Activity for NH<sub>3</sub> Synthesis

The activity of the Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, obtained as described previously, was tested for NH<sub>3</sub> synthesis. The catalyst which was prepared by supporting the Ru colloid on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, showed a remarkably high activity for NH<sub>3</sub> synthesis. The reaction rates expressed as micromoles per gram-hour and turnover frequency (TOF) as a function of temperature are shown in Fig. 7 and Table 3, respectively. Figure 7 shows that the rate of ammonia synthesis over 6.3 wt% Ru/Al<sub>2</sub>O<sub>3</sub> increased progressively with an increase in temperature, reaching a maximum at 723 K. Above this temperature, the rate of the reverse reaction (ammonia decomposition) increased more than the rate of ammonia formation, and therefore the overall rate decreased. The highest reaction rate of 923  $\mu\text{mol g}^{-1} \text{h}^{-1}$  was observed at 723 K. The reproducibility at each reaction temperature was within the range of experimental error ( $\pm 25 \mu\text{mol g}^{-1} \text{h}^{-1}$ ).

TABLE 3

Ammonia Synthesis Catalyzed by 6.3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Prepared by the Polyol Method

Dispersion (%)	TOF ( $10^{-4} \text{S}^{-1}$ )				Ea (kJ/mol)
	638 K	673 K	723 K	773 K	
54	1.4	4.1	7.6	4.9	76.9

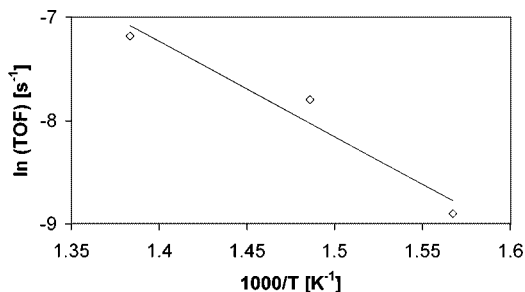


FIG. 8. Arrhenius plot for the ammonia synthesis rate over 6.3 wt% Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The rates (TOF) of ammonia synthesis over Ru nanoparticles supported on alumina are shown in the Arrhenius-type plot in Fig. 8. An apparent activation energy of 76.9 kJ mol<sup>-1</sup> was estimated in Fig. 8 and listed in Table 3. Our result agrees well with the previously published data. The apparent activation energies determined for promoted and nonpromoted Ru/Al<sub>2</sub>O<sub>3</sub> catalysts range between 44 and 101 kJ mol<sup>-1</sup> (3).

From the previous results there are two points that are worthy of note. One is the temperature of highest activity for ammonia synthesis. The highest activity of the conventional Ru/Al<sub>2</sub>O<sub>3</sub> catalysts was observed at 588 K (3), whereas the catalyst prepared from the Ru colloid had a maximum activity at a higher temperature, 723 K. From an industrial point of view, it is preferable for ammonia synthesis to have a catalyst that is more active at a lower temperature. Thermodynamically, the increase in temperature is not favorable for ammonia synthesis reaction. Therefore, it is of great interest to obtain the higher equilibrium conversions at lower temperatures.

The other point is that the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from the Ru colloid showed unusually high activity although it was not promoted. The highest catalytic activities of the promoted and nonpromoted Ru/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by conventional methods using RuCl<sub>3</sub> or Ru<sub>3</sub>(CO)<sub>12</sub> as precursors together with the activity of the catalyst prepared from the Ru colloid are shown in Fig. 7. The reported activity of the nonpromoted conventional Ru/Al<sub>2</sub>O<sub>3</sub> catalysts is very small, ranging from 10 to 65  $\mu\text{mol g}^{-1} \text{h}^{-1}$ . It was reported that the nonpromoted catalysts prepared from RuCl<sub>3</sub> exhibited significantly lower activities as compared to those obtained from Ru<sub>3</sub>(CO)<sub>12</sub>.

The acidity of alumina has been considered the main reason for the low activity of the conventional Ru/Al<sub>2</sub>O<sub>3</sub> catalysts for ammonia synthesis. The addition of alkaline (Cs, Rb, K) or rare earth (La, Ce, La, Sm) elements to Ru/Al<sub>2</sub>O<sub>3</sub> leads to a significant increase in the catalytic activity (2, 21). Typically, the activity of the promoted Ru/Al<sub>2</sub>O<sub>3</sub> catalysts ranges from 130 to 250  $\mu\text{mol g}^{-1} \text{h}^{-1}$  (Fig. 7). The Ru/Al<sub>2</sub>O<sub>3</sub> catalyst prepared from the Ru colloid showed a

significantly higher activity than that from promoted catalysts. A notable exception is the  $K^+$ -promoted  $Ru/Al_2O_3$  catalyst, prepared from  $Ru_3(CO)_{12}$ , whose catalytic activity for ammonia synthesis was reported to be  $2470 \mu\text{mol g}^{-1} \text{h}^{-1}$  under conditions comparable to ours ( $0.4 \text{ g catalyst, } 60 \text{ ml min}^{-1}$ ) (21). However, the activity of the conventionally prepared Ru catalysts is strongly dependent on the conditions of preparation. Slight changes of the preparation variables result in significant changes in the catalytic activity.

The differences observed between the  $Ru/Al_2O_3$  catalysts prepared by the conventional impregnation methods and the catalyst obtained via colloid deposition raise problems regarding the role that supports play in the formation of catalytically active phases. We reported that the support plays an essential role in the formation of the active phase(s) when the catalysts were prepared by the impregnation method (6, 7). The impregnation process can be regarded as complex sequences of chemical reactions taking place at the solid (the support)/liquid (solution of the metal salt) interface. In the case of Cu and Pd, we revealed that a certain amount of alumina is dissolved during the adsorption of the metal precursor even in the neutral pH range. The dissolved aluminium ions together with  $Cu^{2+}$  or  $Pd^{2+}$  ions can reprecipitate on the surface of the support, and thus participate in the formation of active sites.

The variation of the activities of  $Ru/Al_2O_3$  catalysts prepared by conventional impregnation methods has been attributed to various factors such as size distribution of the supported metal particles, support influence on the morphology of the ruthenium crystals (23), and calcination and reduction processes. However, the comparison between the two preparation methods, suggests the possibility that the low and unstable activity of  $Ru/Al_2O_3$  catalysts prepared by conventional impregnation methods is caused not only by the acidity of the support but also by the contamination of the Ru metal by aluminum. It is highly possible that some aluminum is dissolved from the solid during impregnation, and then participates, together with Ru, in the formation of the active sites. On the other hand, in the case of  $Ru/Al_2O_3$  preparation from the Ru colloid, Ru interacts with the support not as ions but as metal particles. The small amount of HCl resulting from the reduction of  $RuCl_3$  with ethylene glycol seems to have little influence on the catalytic activity of  $Ru/Al_2O_3$ . It is clear that the interaction between the support and the Ru nanoparticles is minimized by this preparation method, and therefore the active phase (Ru metal) is not contaminated by aluminum or chlorine ions derived from the support.

During the impregnation process, the metal particles, i.e., the active sites of the catalysts, are contaminated more or less by the supports. In this case the acid or base character of the supports plays an important role in determining the final

catalytic activity. In contrast to the impregnation method, metal colloid deposition onto a support gives metal particles that are uncontaminated by the support. Therefore, the influence of the support on the metallic active phase is minimized. The  $Ru/Al_2O_3$  catalyst prepared in this study is supposed to have Ru metal nanoparticles that do not interact significantly with the support, and this should be the reason for the remarkably high catalytic activity demonstrated for ammonia synthesis.

#### 4. CONCLUSIONS

A stable Ru metal colloid was obtained by reducing  $RuCl_3$  in ethylene glycol. The metal particles in the colloidal solution had a uniform shape and size of 5 nm. The colloidal Ru nanoparticles (up to 6.3 wt%), maintaining their initial morphology, were successfully supported on  $\gamma\text{-}Al_2O_3$ . The  $Ru/\gamma\text{-}Al_2O_3$  prepared from the colloid showed an unusually high activity for ammonia synthesis. The novel preparation method of supported Ru catalysts proposed in this paper has the following advantages: (i) it is relatively easy to control the size and shape of metal particles; (ii) the interaction between the metal particles and the support is minimized, and therefore the metal-active sites are not contaminated by the support.

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